

What is claimed is:

1. A method of producing a nanoporous silica dielectric film comprising
 - (a) preparing a composition comprising a silicon containing pre-polymer, a
5 metal-ion-free catalyst selected from the group consisting of onium
compounds and nucleophiles; and a porogen which does not bond to the
silicon containing pre-polymer;
 - (b) coating a substrate with the composition to form a film,
 - (c) crosslinking the composition to produce a gelled film, and
10 (d) heating the gelled film at a temperature and for a duration effective to
remove substantially all of said porogen.
2. The method of claim 1 wherein the nanoporous silica dielectric film has a
pore void volume of from about 5% to about 80% based on the volume of the
15 film.
3. The method of claim 1 wherein the resulting nanoporous silica dielectric
film has a dielectric constant of about 3 or below.
- 20 4. The method of claim 1 wherein the nanoporous silica dielectric film has an
average pore diameter in the range of from about 1 nm to about 30 nm.
5. The method of claim 1 wherein the porogen is selected from the group
consisting of a poly(alkylene) diether, a poly(arylene) diether, poly(cyclic
25 glycol) diether, Crown ethers, polycaprolactone, fully end-capped
polyalkylene oxides, fully end-capped polyarylene oxides, polynorbene, and
combinations thereof.
6. The method of claim 1 wherein the porogen is selected from the group
30 consisting of a poly(ethylene glycol) dimethyl ether, a poly(ethylene glycol)

- bis(carboxymethyl) ether, a poly(ethylene glycol) dibenzoate, , a poly(ethylene glycol) propylmethyl ether, a poly(ethylene glycol) diglycidyl ether, a poly(propylene glycol) dibenzoate, a poly(propylene glycol) dibutyl ether, a poly(propylene glycol) dimethyl ether, a poly(propylene glycol) diglycidyl ether, 15-Crown 5, 18-Crown-6, dibenzo-18-Crown-6, dicyclohexyl-18-Crown-6, dibenzo-15-Crown-5 and combinations thereof.
- 5
7. The method of claim 1 wherein the catalyst is selected from the group consisting of ammonium compounds, amines, phosphonium compounds, and phosphine compounds.
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8. The method of claim 1 wherein the catalyst is selected from the group consisting of tetraorganoammonium compounds and tetraorganophosphonium compounds.
- 15
9. The method of claim 1 wherein the catalyst is selected from the group consisting of tetramethylammonium acetate, tetramethylammonium hydroxide, tetrabutylammonium acetate, triphenylamine, trioctylamine, tridodecylamine, triethanolamine, tetramethylphosphonium acetate, tetramethylphosphonium hydroxide, triphenylphosphine, trimethylphosphine, trioctylphosphine, and combinations thereof.
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10. The method of claim 1 wherein the composition further comprises a non-metallic, nucleophilic additive which accelerates the crosslinking of the composition.
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11. The method of claim 1 wherein the composition further comprises a nucleophilic additive which accelerates the crosslinking of the composition, which is selected from the group consisting of dimethyl sulfone, dimethyl

formamide, hexamethylphosphorous triamide, amines and combinations thereof.

12. The method of claim 1 wherein the composition further comprises water
5 in a molar ratio of water to said Si atoms in said silicon containing prepolymer ranging from about 0.1:1 to about 50:1.

13. The method of claim 1 wherein the composition comprises a silicon containing prepolymer of Formula I:

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$$R_x - Si - L_y \quad \text{(Formula I)}$$

wherein x is an integer ranging from 0 to about 2, and y is 4-x, an integer ranging from about 2 to about 4;

R is independently selected from the group consisting of alkyl, aryl, hydrogen, alkylene, arylene, and combinations thereof;

15 L is an electronegative moiety, independently selected from the group consisting of alkoxy, carboxy, amino, amido, halide, isocyanato and combinations thereof.

14. The method of claim 13 wherein the composition comprises a polymer
20 formed by condensing a prepolymer according to Formula I, wherein the number average molecular weight of said polymer ranges from about 150 to about 300,000 amu.

15. The method of claim 1 wherein the composition comprises a silicon
25 containing pre-polymer selected from the group consisting of an acetoxysilane, an ethoxysilane, a methoxysilane, and combinations thereof.

16. The method of claim 1 wherein the composition comprises a silicon containing pre-polymer selected from the group consisting of

tetraacetoxysilane, a C₁ to about C₆ alkyl or aryl-triacetoxysilane, and combinations thereof.

17. The method of claim 16 wherein said triacetoxysilane is
5 methyltriacetoxysilane.

18. The method of claim 1 wherein the composition comprises a silicon
containing pre-polymer selected from the group consisting of tetrakis(2,2,2-
trifluoroethoxy)silane, tetrakis(trifluoroacetoxy)silane, tetraisocyanatosilane,
10 tris(2,2,2-trifluoroethoxy)methylsilane, tris(trifluoroacetoxy)methylsilane,
methyltriisocyanatosilane and combinations thereof.

19. The method of claim 1 wherein the step (c) crosslinking is conducted at a
temperature which is less than the heating temperature of step (d).
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20. The method of claim 1 further comprising an additional porogen wherein
the additional porogen has a boiling point, sublimation point or decomposition
temperature ranging from about 150°C to about 450°C.

21. The method of claim 1 wherein heating step (c) comprises heating the
film at a temperature ranging from about 100 °C to about 250°C, for a time
period ranging from about 30 seconds to about 10 minutes.
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22. The method of claim 1 wherein step (d) comprises heating the film at a
25 temperature ranging from about 150 °C to about 450 °C, for a time period
ranging from about 30 seconds to about 1 hour.

23. The method of claim 1 further comprising an additional porogen wherein
the additional porogen has a molecular weight ranging from about 100 to
30 about 50,000 amu.

24. The method of claim 1 further comprising an additional porogen wherein the additional porogen comprises a reagent comprising at least one reactive hydroxyl or amino functional group, and said reagent is selected from the group consisting of an organic compound, an organic polymer, an inorganic polymer and combinations thereof.

25. The method of claim 1 further comprising an additional porogen wherein the additional porogen is selected from the group consisting of a polyalkylene oxide, a monoether of a polyalkylene oxide, an aliphatic polyester, an acrylic polymer, an acetal polymer, a poly(caprolactone), a poly(valeractone), a poly(methyl methacrylate), a poly (vinylbutyral) and combinations thereof.

26. The method of claim 1 further comprising an additional porogen wherein the additional porogen comprises a polyalkylene oxide monoether which comprises a C₁ to about C₆ alkyl chain between oxygen atoms and a C₁ to about C₆ alkyl ether moiety, and wherein the alkyl chain is substituted or unsubstituted.

27. The method of claim 26 wherein the polyalkylene oxide monoether is a polyethylene glycol monomethyl ether or polypropylene glycol monobutyl ether.

28. The method of claim 1 wherein the porogen is present in the composition in an amount of from about 1 to about 50 percent by weight of the composition.

29. The method of claim 1 wherein the composition further comprises a solvent.

30. The method of claim 1 wherein the composition further comprises solvent in an amount ranging from about 10 to about 95 percent by weight of the composition.

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31. The method of claim 1 wherein the composition further comprises a solvent having a boiling point ranging from about 50 to about 250 °C.
32. The method of claim 1 wherein the composition further comprises a solvent selected from the group consisting of hydrocarbons, esters, ethers, ketones, alcohols, amides and combinations thereof.
33. The method of claim 29 wherein the solvent is selected from the group consisting of di-n-butyl ether, anisole, acetone, 3-pentanone, 2-heptanone, ethyl acetate, n-propyl acetate, n-butyl acetate, 2-propanol, dimethyl acetamide, propylene glycol methyl ether acetate, and combinations thereof.
34. A nanoporous dielectric film produced on a substrate by the method of claim 1.
35. A semiconductor device comprising a nanoporous dielectric film of claim 34.
36. The semiconductor device of claim 35 that is an integrated circuit.

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37. A composition comprising a silicon containing pre-polymer, a metal ion free catalyst, and a porogen that does not bond to the silicon containing pre-polymer and is selected from the group consisting of poly(alkylene) diether, a poly(arylene) diether, poly(cyclic glycol) diether, Crown ethers, polycaprolactone, fully end-capped polyalkylene oxides, fully end-capped polyarylene oxides, polynorbene, and combinations thereof.

38. The composition of claim 37 wherein said metal-ion-free catalyst is tetramethylammonium acetate.

39. The composition of claim 37 wherein said silicon containing pre-polymer comprises a combination of acetoxy-based leaving groups.

40. The composition of claim 39 wherein said combination of acetoxy-based leaving groups comprises tetraacetoxysilane and methyltriacetoxysilane.

41. A spin-on composition comprising said composition of claim 37.

42. A film comprising said spin-on composition of claim 41.

43. In a method of controlling the pore size of a porous silica film, comprising